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I - REACTIONS OF SILANE, GERMANE AND STANNANE WITH METAL- AND AMIDE-AMMONIA SOLUTIONS

II - PREPARATION AND REACTIONS OF POTASSIUM GERMYLTRIHYDROBORATE, $KGeH_3BH_3$

Douglas Scott Rustad

June 1967

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Part I

REACTIONS OF SILANE, GERMANE AND STANNANE WITH METAL- AND AMIDE-AMMONIA SOLUTIONS

Douglas S. Rustad

Inorganic Materials Research Division, Lawrence Radiation Laboratory, and the Department of Chemistry, University of California, Berkeley, California

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ABSTRACT

Germane reacts with liquid ammonia solutions of potassium or potassium amide at -77° to form potassium germyl, germanium imide, and hydrogen gas. The fraction of the germane converted to germanium imide increases with increasing potassium concentration, but remains constant with increasing potassium amide concentration. Amide ion is an intermediate in the reaction of germane with metal-ammonia solutions. In the case of silane, the main reaction is ammonolysis, whereas in the case of stannane, no ammonolysis occurs. A general mechanism is proposed to explain the results.

A. Introduction

It has been reported by Kraus and his coworkers[1,2] that sodium germyl ($NaGeH_3$) and potassium germyl ($KGeH_3$) can be prepared quantitatively by passing germane through liquid ammonia solutions of the appropriate metals.

$$e^- + GeH_4 \rightarrow GeH_3^- + 1/2\ H_2 \qquad (1)$$

However, when Emeléus and Mackay[3] conductimetrically titrated sodium-ammonia solutions with germane, hydrogen gas in excess of that required by Equation 1 was evolved. Early attempts in this laboratory to prepare pure potassium germyl also failed, as evidenced by excess hydrogen gas evolution.[4] Because of these conflicting results, we have reinvestigated the reaction of germane with metal-ammonia solutions. We have studied the effects, on the amount of excess hydrogen gas evolved, of varying (a) the metal concentration, (b) the amide concentration, and (c) the method of mixing the reagents. Less extensive, but comparable, studies of silane and stannane have also been carried out. From the results of these studies, we propose a mechanism for the reactions.

B. Experimental

1. General

Standard vacuum line techniques were employed in handling volatile materials. Non-condensible gases were collected and measured using a Toepler pump.

Ammonia (Jones Chemicals, Inc.) was purified with potassium. Potassium and sodium were distilled directly into the reactor *in vacuo*. Silane[5] and germane[6] were prepared and purified by standard methods. Stannane

was generously supplied by Mr. John Webster. Methyl chloride (Matheson Co., Inc.) was purified by fractional distillation. Granular anhydrous magnesium perchlorate was obtained from Matheson, Coleman and Bell.

The identity and purity of the volatile materials were determined by infrared spectrometry with Perkin-Elmer Infracord spectrophotometers (Models 137B and 137), by mass spectrometry with a Consolidated Engineering Corporation Mass Spectrometer Model 21-620, by molecular weight determinations and by vapor pressure measurements.

Germanium was determined volumetrically[7] and chloride was determined gravimetrically.

2. Typical Procedures

A typical reaction vessel was constructed from a 2.5 × 14 cm Pyrex tube, sealed at one end, with two stopcocks attached in series at the other end. Two sealed side-arms were attached, one between the two stopcocks, and the other directly to the tube. A still for sodium or potassium, consisting of a bent 1.0 × 10 cm sealed tube, was connected to the tube via a constriction.

An approximately known amount of metal was distilled into the main section. The constriction was closed, and the still removed. A measured volume of liquid ammonia was then distilled in, and the metal was washed from the walls by refluxing the ammonia.

When amide was required, it was prepared by lowering a rusty nail from the tube's side-arm into the metal-ammonia solution. In order to achieve a reasonable reaction rate, it was necessary to warm the solution to about -20°. The amount of amide was determined from the hydrogen gas evolved.

A measured amount of hydride (GeH_4, SiH_4 or SnH_4) was condensed onto the metal- or amide-ammonia solid at -196°. The reaction mixture was allowed to warm rapidly in air until all of the ammonia just melted (about -77°), and reaction was allowed to proceed at this temperature. A dry ice-acetone bath was used as a coolant. The reaction mixture was either shaken continually or not at all during the reaction.

In an alternative method, the hydride was condensed into the side-arm between the two stopcocks. With the metal-ammonia solution at -77°, the lower stopcock was opened completely, and the gaseous hydride was allowed to expand into the main section and react with the liquid solution.

At the completion of the reaction the mixture was cooled to -196°, and hydrogen gas was measured. The reactor was then warmed to -77°, and the excess hydride was removed and measured.

3. Germane Experiments

After the removal of hydrogen gas and excess germane, either water or methyl chloride was added and the mixture was warmed to room temperature or -77°, respectively. After the completion of the water reaction, germane was removed from the reactor, purified by trap to trap distillation or by passage through granular anhydrous magnesium perchlorate, and measured. In the case of the methyl chloride reaction, the ammonia solvent, excess methyl chloride and methylgermane were distilled from the reactor together. The ammonia was removed by passing the mixture through granular anhydrous magnesium perchlorate. The methylgermane was removed from the excess methyl chloride by letting the mixture stand over iodine at room temperature,[8] passing the resulting material through a -112° trap (carbon disulfide slush) to remove any iodogermanes, and then washing the excess methyl chloride with a sodium hydroxide solution at room temperature to remove

hydrogen iodide.

After the removal of the methylgermane, excess methyl chloride and ammonia solvent, the solid residue was heated with a flame, and the evolved ammonia was measured. A dilute sodium hydroxide solution was then added, and the further evolved ammonia was purified and measured. In another experiment the reactor was not heated; instead, a dilute potassium hydroxide solution was added. The evolved ammonia was processed as before. The solution left in the reactor was analyzed for germanium and chloride.

4. Silane Experiments

The procedures were similar to those of the germane experiments.

5. Stannane Experiments

After the removal of the initial hydrogen gas, the ammonia solvent and excess stannane were removed while Toepler-pumping hydrogen gas from the decomposition of stannane and potassium stannyl ($KSnH_3$). The reactor was heated with a flame until the evolution of hydrogen gas ceased. Water was added to the reactor, and hydrogen gas evolved was measured. Excess stannane was separated from the ammonia by passing the mixture through granular anhydrous magnesium perchlorate.

6. Isolation of Sodium Amide as an Intermediate in the Germane-Sodium-Ammonia Reaction

A little less than half the equivalent of germane was added to a sodium-ammonia solution at -77°. After removal of the hydrogen gas, the blue solution was decanted from the white precipitate into a side-arm. The precipitate was washed with distilled ammonia from the mother liquid. The side-arm containing the mother liquid was then removed from the

reactor. The reactor was opened in a polyethylene dry bag, and x-ray powder samples were prepared. The x-ray powder pattern was obtained by Mrs. Helena Ruben (Lawrence Radiation Laboratory, Berkeley) and was found to be that of sodium amide, by comparison of the pattern with that of an authentic sample of sodium amide.

7. Attempted Reaction of the Electron with Germyl

Potassium (0.450 mmole) was added to 0.526 mmole of potassium germyl in liquid ammonia. During one half-hour at -77°, 0.008 mmole of hydrogen gas was evolved; another half-hour at -45° (chlorobenzene slush) yielded 0.005 mmole. These results are similar to those of Teal and Kraus.[2]

8. Reaction of Potassium Amide with Germyl

The reaction vessel consisted of two identical reactors, similar to that described above except smaller in size, separated by a break-off seal. Potassium amide (1.30 mmoles) was prepared in one of the reactors, and potassium germyl (0.974 mmole) was prepared in the other. Potassium amide formed a yellowish-green solution with no precipitate under the same conditions used during the main reaction, while potassium germyl formed a colorless solution with no precipitation. The break-off seal was broken with a glass-encased metal breaker, and the potassium amide was transferred into the potassium germyl reactor. The rusty nail was held in the amide reactor by a magnet. The initial concentration of potassium germyl in the reaction mixture was 0.362 molal and that of potassium amide was 0.484 molal. The mixture was held at -77° for a half hour. A trace of hydrogen gas was evolved and the color of the solution remained yellowish-green. No precipitate was formed. The mixture was held at 0° for another half hour. The amount of hydrogen gas evolved was 0.099 mmole. The color

of the solution was still yellowish-green. A slight trace of dark precipitate was visible.

9. Germane-Potassium-Ammonia Reaction at -130°, -112° and -77°

Germane (8.94 mmoles) was condensed onto a 2.28 molal potassium-ammonia solution at -196°. The mixture was warmed to -130° (n-pentane slush) and held at this temperature for ten minutes. During this time there was no hydrogen gas evolution. When the mixture was further warmed to -112° and held for ten minutes, hydrogen gas was evolved. Consequently, the mixture was held at -112° for about an hour, during which time the reaction ceased. A white crust was formed over the blue solid, and 1.18 mmoles of hydrogen gas was evolved. Finally, the mixture was warmed to -77° where the rest of the hydrogen gas (1.26 mmoles) was evolved in two minutes. The total amount of reacted germane was 4.19 mmoles.

C. Results

1. Reactions of Germane with the Electron

The results are presented in Table I. The hydrogen gas evolved in excess of that required by Equation 1, expressed as a percentage of the expected hydrogen gas, is tabulated in column 4. For Runs 1-7, and also for Runs 8-10, the percentage excess hydrogen gas increased with increasing concentration of potassium. It is interesting, although of unknown significance, that for the two sets of runs the logarithm of the percentage excess hydrogen gas is linear with the potassium concentration. At very low electron concentrations potassium germyl was obtained almost quantitatively. This agrees with the results of Teal and Kraus,[2] who worked with very low metal concentrations. At about 0.2 molar metal,

Table I. Reactions of Germane with Potassium-Ammonia Solutions at -77°

	1	2	3	4	5	6	7	8	9	10	11
Run	e^- conc.,[f] molal.	GeH_4 reacted, mmoles	H_2 evolved, mmoles	% excess H_2	$Ge(NH)_2$ calcd, mmoles	GeH_3^- calcd, mmoles	GeH_4, H_2O rx., mmoles	Ch_3GeH_3, CH_3Cl rx., mmoles	GeO_3^{--}, mmoles	Cl^-, mmoles	$\frac{Ge(NH)_2}{GeH_3^-}$
1[a]	2.38	6.18	4.30	39.2	0.346	5.83		5.90	0.335	5.86	0.0594
2[a,b]	2.02	5.15	3.28	27.2	0.200	4.95		4.94		4.96	0.0404
3[a,b]	1.55	4.28	2.51	17.3	0.108	4.17	4.11			4.07[c]	0.0259
4[a]	0.99	3.28	1.84	12.2	0.057	3.22					0.0177
5[a]	0.39	2.40	1.27	5.80	0.020	2.38		2.35			0.0084
6[a]	0.11	1.12	0.586	4.80	0.008	1.11					0.0072
7[a]	0.00842	0.272	0.138	1.47							
8[d]	1.93	3.62	2.88	59.1	0.310	3.31	3.32				0.0936
9[d]	1.19	1.44	0.986	37.0	0.076	1.36					0.0559
10[d]	0.44	1.22	0.769	25.8	0.045	1.18	1.15				0.0382
11[d,b]	0.32	1.07	0.711	32.4	0.050	1.02	0.995				0.0490
12[d,e]	1.08	2.10	1.28	21.9	0.066	2.03	2.03				0.0325

[a] Germane and the metal-NH_3 solution were warmed together from -196° to -77°.

[b] Not shaken.

[c] Hydroxide.

[d] Gaseous GeH_4 reacted with the liquid metal-NH_3 solution at -77°.

[e] Na was used. In the others, K was used.

[f] Exact initial electron concentrations were calculated assuming that initial electron concentration was equivalent to the final germyl concentration (Equation 1).

approximately 6% excess hydrogen gas was evolved, in agreement with Emeléus and Mackay's results.[3]

It is significant that, for a given metal concentration, the percentage excess hydrogen gas increased with the reaction temperature. Thus in the run described under Experimental in which the reactants (GeH_4 + 2.28 molal K) were held at -112° before warming to -77°, 16.2% excess hydrogen gas was evolved. From the data in Table I, we would expect that if these reactants had been warmed with relative rapidity to -77 , about 35% excess hydrogen gas would have been evolved, and that if the gaseous germane had reacted directly at -77 , more than 60% excess hydrogen gas would have been evolved.

The time for the blue color to fade in shaken solutions ranged from 2 to 5 minutes, depending on concentration. For unshaken solutions the time was about 1.5 hours, and two-layer systems formed - colorless on top and blue on the bottom. The thickness of the blue layer slowly decreased with time. Apparently under these conditions the overall rate of reaction is diffusion-controlled.

In all of the runs in Table I (except 6 and 7) a white precipitate formed. The amount of this precipitate was markedly greater for the runs of higher metal concentration. On the basis of evidence which we describe below, we believe that this precipitate was germanium imide, $Ge(NH)_2$ (or possibly germanium tetraamide, $Ge(NH_2)_4$), and that the side reaction (Equation 2) yielding this product was responsible for the excess hydrogen gas observed.

$$GeH_4 + 2NH_3 \rightarrow Ge(NH)_2 + 4H_2 \qquad (2)$$

2. Evidence for $Ge(NH)_2$ or $Ge(NH_2)_4$

With the addition of an excess of either methyl chloride or water to the reaction products, there was no methane or hydrogen gas evolution. The chloride ion formed in the reaction of methyl chloride was equivalent to the methylgermane evolved, and the hydroxide ion formed in the reaction of water was equivalent to the germane evolved. No hydrogen gas was formed on heating the reactor after removal of the methylgermane. We conclude that reactions 3 and 4 proceed quantitatively without formation of polymeric germanium hydride[9] or potassium hydride.

$$GeH_3^- + H_2O \rightarrow GeH_4 + OH^- \qquad (3)$$

$$GeH_3^- + CH_3Cl \rightarrow CH_3GeH_3 + Cl^- \qquad (4)$$

Thus we may take the volatile products of these reactions (columns 7 and 8, Table I) as measures of the potassium germyl present. If we assume that reactions 1 and 2 are the only net reactions undergone by the germane, then the amount of potassium germyl formed may be calculated independently from the data of columns 2 and 3 (Table I). These calculated amounts of potassium germyl are given in column 6, and it can be seen that there is good agreement with the values in columns 7 and 8. The data show that the side-reaction in the reaction of germane with a potassium-ammonia solution involves the evolution of four moles of hydrogen gas per mole of germane consumed.

Germanium tetraamide apparently has never been isolated. Thomas and Pugh[10] attempted to isolate it at -20°, but obtained only the imide, $Ge(NH)_2$. Because our reaction mixtures were ultimately warmed to room temperature, we would not expect to have obtained the amide, even if it

had formed at the lower temperature. We shall hereafter arbitrarily refer to the precipitate as the imide, with the understanding that it initially may have been the amide. Our subsequent arguments are not affected by this decision.

In runs 1 and 2, Table I, the final white precipitate was treated as described under Experimental, Germane Experiments. In run 1 the solid was heated, and 0.164 mmole of ammonia was evolved. Subsequent treatment with a dilute sodium hydroxide solution liberated 0.498 mmole of ammonia. Germanium analysis gave 0.335 mmole. These results agree with reactions 5 and 6.[10,11]

$$2Ge(NH)_2 \rightarrow Ge_2N_3H + NH_3 \qquad (5)$$

$$Ge_2N_3H + 4OH^- + 2H_2O \rightarrow 2GeO_3^{2-} + 3NH_3 \qquad (6)$$

Anal. Calcd Ge (from column 5, Table I): 0.346 mmole. Found: 0.335 mmole.

Calcd NH_3 for reaction 5: 0.167 mmole. Found: 0.164 mmole.

Calcd NH_3 for reaction 6: 0.501 mmole. Found: 0.498 mmole.

In run 2 treatment with a dilute potassium hydroxide solution liberated 0.396 mmole of ammonia. This result agrees with reaction 7.[10,11]

$$Ge(NH)_2 + 2OH^- + H_2O \rightarrow GeO_3^{2-} + 2NH_3 \qquad (7)$$

Anal. Calcd NH_3 (from column 5, Table I): 0.400 mmole. Found: 0.396 mmole.

3. Titrations of Potassium-Ammonia Solutions with Germane

Gaseous germane was added in small increments to a potassium-ammonia solution at -77°. After each addition the hydrogen gas was measured. The

results for two titrations are presented in Figure 1. The blue color of the electron in the 0.63 molal solution disappeared between the Σ GeH_4/ initial e^- ratios of 0.55 and 0.67. At this point the color of the solution changed to light yellowish-green which upon further addition of germane slowly faded. The solution became colorless between the Σ GeH_4/ initial e^- ratios of 1.03 and 1.15. The amount of white precipitate increased with each addition after the electron end point. The solution was too opaque to see any precipitate before this end point. Too large increments were used for the 0.43 molal solution titration. Consequently, no significant observations similar to the above were obtained. It is clear that the course of the reaction is altered upon going from the procedure of the runs in Table I to the titration procedure. From Table I a 0.43 molal solution should give about 25% excess hydrogen gas compared to the 84.8% observed, and a 0.63 molal solution should give about 28% compared to 102%. An explanation of these results are given in the Discussion.

4. Reactions of Gaseous Germane with Potassium Amide-Ammonia Solutions at -77°

The results are presented in Table II. The germane evolved when excess water was added to the reaction products (column 7, Table II) can be taken as a measure of the potassium germyl present (Equation 3). We see that this germane evolved was equivalent to the initial amide, and that the evolved hydrogen gas (column 4, Table II) was four times the amount of reacted germane not involved in the formation of potassium germyl. Thus the results are consistent with the simultaneous occurrence of reactions 2 and 8.[2]

$$GeH_4 + NH_2^- \rightarrow GeH_3^- + NH_3 \qquad (8)$$

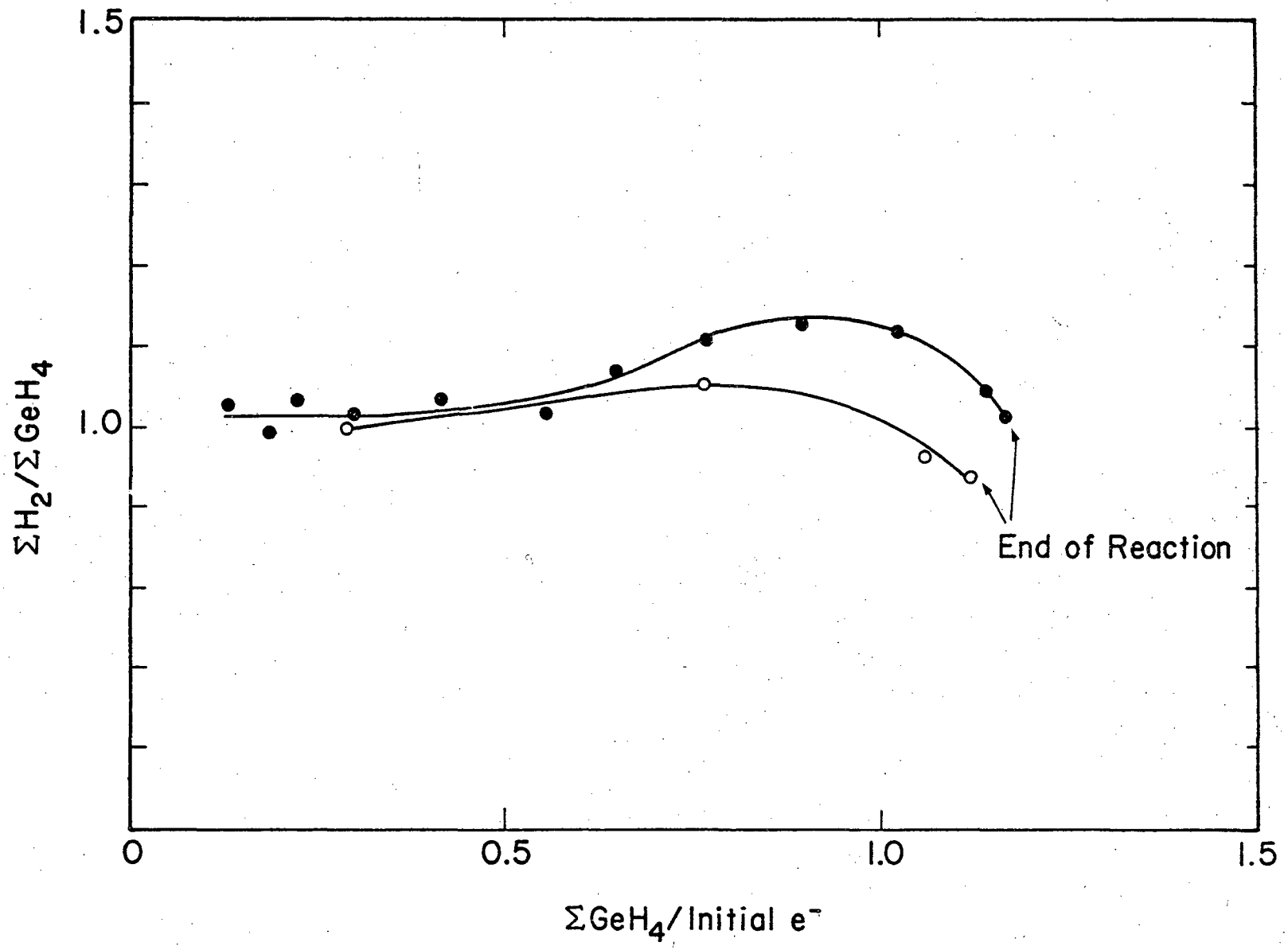

Fig. I-1 Titrations of potassium-ammonia solutions with germane at -77°. Open circles refer to run with 0.43 molal potassium (0.383 mmole K), 84.8% excess H_2. Solid points refer to run with 0.63 molal potassium (0.870 mmole K), 102% excess H_2.

Table II. Reactions of Gaseous Germane and Potassium Amide-Ammonia Solutions at -77°

	1	2	3	4	5	6	7	8
Run	NH_2^- conc., molal	NH_2^-, mmole	GeH_4 reacted, mmole	H_2[b] evolved, mmole	GeH_3^- calcd, mmole	$Ge(NH)_2$ calcd, mmole	GeH_4 H_2O rx., mmole	$\frac{Ge(NH)_2}{GeH_3^-}$
1	0.526[a]	2.00	2.31	1.41	1.96	0.352	1.96	0.180
2	0.194	0.896	1.03	0.631	0.870	0.158	0.868	0.181
3	<0.0055	<0.005	<0.005	trace				

[a] Maximum solubility.

[b] The time for the hydrogen gas evolution to cease with shaking varied from 2 to 7 minutes.

5. Reactions of Silane with a Potassium Amide-Ammonia Solution

A mixture of 0.628 mmole of silane and a 0.011 molal potassium amide-ammonia solution (0.010 mmole of amide) was warmed to -77° from -196°. The reaction was allowed to proceed at this temperature for 16.5 hours. During this time there was slow bubbling, and the solution was clear and colorless, with no precipitate. Hydrogen gas (2.48 mmoles) was evolved and all of the silane reacted. The ammonia solvent was then removed, and the white solid residue was warmed with a low flame until ammonia evolution ceased. With the addition of a dilute sodium hydroxide solution, 0.033 mmole of hydrogen gas and 1.30 mmoles of ammonia were evolved.

The amount of initial hydrogen gas was about four times the amount of silane reacted, and ammonia was evolved when the residue was warmed and when an alkaline solution was added. These results are indicative of silicon imide formation.[11,12,13] Since there was also hydrogen gas evolution when the alkaline solution was added, potassium silyl ($KSiH_3$) or incompletely ammonolyzed silane was probably present.

Anal. Calcd total H_2 from SiH_4 reacted: 2.51 mmoles. Found: 2.51 mmoles
Calcd NH_3 from hydrolysis as $Si(NH)_2$: 1.26 mmoles. Found: 1.30 mmoles.

6. Reactions of Silane with a Potassium-Ammonia Solution

Silane (6.42 mmoles) was condensed onto a 0.05 molal potassium solution (1.4 mmoles of K) at -196°. The reaction vessel was warmed in air to -77°. There was slow bubbling for 1.5 hours (the solution was shaken occasionally), and during this time all of the silane reacted. During and after the reaction, the color of the solution remained blue. The

amount of hydrogen gas evolved was 21.88 mmoles. The H_2/SiH_4 ratio was 3.41. Some more silane (9.55 mmoles) was then condensed into the reactor and allowed to react as before. There was slow bubbling which ceased after seven hours; the silane was completely consumed. The blue color faded during this time and a small amount of gray precipitate was formed. The amount of hydrogen gas evolved was 38.70 mmoles, corresponding to a H_2/SiH_4 ratio of 4.05. Again, some more silane (1.06 mmoles) was condensed into the reactor and allowed to react as before. During four hours 4.68 mmoles of hydrogen gas was evolved and all of the silane reacted, corresponding to a H_2/SiH_4 ratio of 4.41. There was still a very slow evolution of hydrogen gas from the solution. No change in the gray precipitate was visible. After adding methyl chloride (3.21 mmoles) to the final reaction mixture at -196° and warming in air to -77°, a vigorous reaction took place. Methane (0.113 mmole), hydrogen gas (0.846 mmole), a trace of methylsilane and unreacted methyl chloride (2.51 mmoles) were removed from the reaction mixture.

Since the overall H_2/SiH_4 ratio was 3.83 and a large excess of silane was required to remove all the metal, ammonolysis of silane was the main reaction. Silane reacted with the solution even after all of the metal had reacted, indicating that amide was still present. The initial reaction yielded a H_2/SiH_4 ratio of 3.41 and the overall ratio was 3.83 which suggest the formation of potassium silyl. Since the H_2/SiH_4 ratios increased to above four and there was a very slow hydrogen gas evolution from the final reaction mixture, potassium silyl was probably being slowly ammonolyzed. These results are similar to those of Isenberg.[12] He prepared potassium silyl, indicated by the formation of methylsilane, but he was not able to isolate it because of ammonolysis. The methane and

hydrogen gas evolution after methyl chloride addition probably arose from the ammonolysis of the methylsilane, because only a trace of methylsilane was recovered.

7. Reaction of Stannane with a Potassium Amide-Ammonia Solution

A mixture of 0.605 mmole of stannane and a 0.49 molal potassium amide-ammonia solution (0.416 mmole of amide) was warmed to -77° from -196°. Tin mirrors formed on the uncooled parts of the reactor immediately. The final solution was colorless and contained a small amount of gray precipitate. Initial hydrogen gas from the decomposed stannane was 0.280 mmole. The hydrogen gas evolved during the removal of the ammonia and excess stannane and subsequent heating was 0.727 mmole. After heating, the reactor contained tin mirrors and a black powder. With water addition, 0.200 mmole of hydrogen gas was liberated and the black powder turned gray. Unreacted stannane (0.006 mmole) was removed from the ammonia.

These results agree with Equations 9, 10, 11,[15] and 12.[15]

$$SnH_4 \rightarrow Sn + 2H_2 \qquad (9)$$

$$SnH_4 + NH_2^- \rightarrow SnH_3^- + NH_3 \qquad (10)$$

$$KSnH_3 \rightarrow KSn + 3/2\ H_2 \qquad (11)$$

$$KSn + H_2O \rightarrow KOH + Sn + 1/2\ H_2 \qquad (12)$$

Anal. Calcd H_2 from SnH_4 reacted: 1.198 mmoles. Found: 1.207 mmoles.

D. Discussion

1. Germane

The germane mechanism will be discussed in detail. The reactions of silane and stannane will then be discussed in terms of this mechanism.

Emeléus and Mackay[3] found a minimum in their conductimetric titration curves for the reaction of germane with sodium-ammonia solutions at -63°. This minimum corresponded to the electron end point and a GeH_4/Na ratio of about 0.6. They stated that at the minimum there was a yellowish solution and a yellowish-green precipitate. They concluded that the precipitate was sodium germylene (Na_2GeH_2). The increase in conductance after the electron end point was explained by the subsequent reaction of germane with the germylene to form germyl. Also, the increase in conductance with increase in temperature was explained by the reaction of germylene with ammonia to form germyl and amide.

In our study, the intermediate white precipitate was found to be sodium amide. All of the observations, except the yellowish-green color of the precipitate of Emeléus and Mackay, can be explained by using sodium amide. The initial decrease in conductivity in Emeléus and Mackay's titrations was caused by the disappearance of the highly conducting ammoniated electrons. The subsequent rise in conductivity is attributable to the production of ions by the reaction

$$NaNH_2 + GeH_4 \rightarrow Na^+ + GeH_3^- + NH_3 \qquad (13)$$

The solubility of sodium amide increases with increasing temperature,[16] and this can explain the increase in conductivity in the region of the minimum with increasing temperature. Amide solutions are colorless to

yellowish-green, depending on the concentration and temperature. The higher the concentration and the temperature, the more intense the coloration becomes. Potassium amide is soluble in liquid ammonia at -77° (2.9 g/100 g), and consequently it does not precipitate during the reaction of germane with potassium-ammonia solutions.

It seems clear that the reaction of germane with metal-ammonia solutions involves the formation of significant amounts of metal amide and germanium imide. In order to account for these facts we propose the following mechanism:

$$e^- + GeH_4 \rightarrow [GeH_4^-] \rightarrow GeH_3^- + H \qquad (14)$$

$$H + e^- \rightarrow H^- \qquad (15)$$

$$H^- + NH_3 \rightarrow NH_2^- + H_2 \qquad (16)$$

$$2H \rightarrow H_2 \qquad (17)$$

$$GeH_4 + NH_2^- \rightarrow GeH_3^- + NH_3 \qquad (8)$$

$$GeH_4 + NH_2^- \rightarrow GeH_3NH_2 + H^- \qquad (18)$$

The formation of hydride ion as an intermediate seems plausible because when potassium silyl ($KSiH_3$) is prepared from the reaction of silane with potassium in 1,2-dimethoxyethane, potassium hydride is formed as a by-product.[14] The ratio of the rate of reaction 15 to the rate of reaction 14 is given in Equation 19.

$$Rate_{15}/Rate_{14} = k_{15}[H]/k_{14}[GeH_4] \qquad (19)$$

The steady state concentration for hydrogen atoms can be derived, Equations 20 and 21.

$$\frac{d[H]}{dt} = k_{14}[e^-][GeH_4] - k_{15}[H][e^-] - 2k_{17}[H]^2 \simeq 0 \qquad (20)$$

$$[H] = \left(k_{15}\sqrt{k_{15}^2[e^-]^2 + 8k_{14}k_{17}[e^-][GeH_4]} - k_{15}^2[e^-]\right)\Big/4k_{17} \qquad (21)$$

Combining Equations 19 and 21, the expression for the ratio of the rates is then given in Equation 22.

$$\frac{Rate_{15}}{Rate_{14}} = \left(k_{15}\sqrt{k_{15}^2[e^-]^2 + 8k_{14}k_{17}[e^-][GeH_4]} - k_{15}^2[e^-]\right)\Big/4k_{14}k_{17}[GeH_4] \qquad (22)$$

The concentration of germane is assumed to be constant throughout most of the reaction since germane was in excess. Also the rate of reaction 16 is assumed to be very fast since ammonia is in large excess. From this ratio, one would expect the rates of reactions 15 and 16, relative to the rate of reaction 14, to increase with increasing metal concentration. Thus the total integrated amount of amide formed per mole of metal consumed would increase with increasing metal concentration.

We have shown that, in the germane-amide reactions, the $Ge(NH)_2/GeH_3^-$ ratio is constant and independent of the amide concentration (Table II), and that amide ion acts as a catalyst in the formation of germanium imide. Reactions 8, 16 and 18 are consistent with these observations.[17] Because reactions 8 and 18 involve the same reactants, the ratio of their rates would be a constant. The mechanism predicts that at higher metal concentrations and therefore higher total integrated amount of amide a larger fraction of the germane would be consumed by reactions 8 and 18,

and consequently a larger fraction of the germane would undergo ammonolysis to $Ge(NH)_2$. Thus, we have an explanation of the fact that the percentage of excess hydrogen gas evolved increases with increasing metal concentration.

In the titrations of potassium-ammonia solutions, potassium was in excess during the first part of the titrations. One would expect from the above mechanism that the rate of reaction 15 relative to the rate of reaction 14 would be greater with excess potassium than with excess germane. The total integrated amount of amide formed, and consequently the amount of ammonolysis, would be greater in the titrations than in the experiments with excess germane. This explains the extraordinarily large amount of excess hydrogen gas formed during the titrations.

It has been shown that the germyl ion is essentially inert toward the electron. However, it is conceivable that during the reaction of germane with a potassium solution the amide ions might react with germyl ions to form a significant concentration of germylene ions, GeH_2^{2-}.

$$NH_2^- + GeH_3^- \rightleftharpoons NH_3 + GeH_2^{2-} \qquad (23)$$

Divalent anion salts generally are insoluble in liquid ammonia,[19] and it is conceivable that the initial unwashed precipitate which formed in the germane-potassium-ammonia reactions was a mixture of K_2GeH_2 and $Ge(NH)_2$. To check on this possibility a solution of potassium amide was added to a solution of potassium germyl. Potassium amide was in excess, and the volume of liquid ammonia was adjusted so that potassium amide was near its solubility limit at -77°. No significant amount of precipitation occurred either at -77° or at temperatures up to 0°. There was a small

amount of hydrogen gas evolved, probably from the amide-catalyzed ammonolysis of the germyl ion. In a separate n.m.r. study[20] involving similar concentrations of amide ion and germyl ion at room temperature, the n.m.r. peak for the germyl ion and a single sharp peak for ammonia and amide ion were visible, but there were no indications of the presence of the germylene ion. These data make it unlikely that the germylene ion is capable of existence in liquid ammonia in significant concentrations.

2. Silane

We have observed that silane is extensively ammonolyzed by an amide solution, even at a very low amide concentration. Now this does not mean that the rate constant for the reaction analogous to reaction 18 is necessarily greater than that for the analog of reaction 8. Indeed, because both silane and germane are more acidic than ammonia, it is possible that reaction 8 and the analogous reaction of silane are nearly diffusion-controlled. An explanation for the extensive ammonolysis in the case of silane can be found in the fact that silane is a considerably weaker acid than germane. The amide ion in equilibrium with a silyl solution is probably responsible for the instability of the solution.

$$SiH_3^- + NH_3 \rightleftharpoons SiH_4 + NH_2^- \qquad (24)$$

Germane is a relatively strong acid, and consequently the equilibrium concentration of amide ion in a germyl solution is too small to catalyze the ammonolysis.

3. Stannane

We found no evidence for ammonolysis in the reaction of stannane

with amide solutions. We therefore conclude that the stannane analog of reaction 18 is a relatively slow reaction.

4. Summary

The mechanism described above satisfactorily accounts for the various unusual features of the reaction of germane with metal-ammonia solutions and explains why apparently conflicting results have been obtained by previous investigators. This same mechanism is applicable to the analogous reactions of silane and stannane if we assume that, on going from SiH_4 to GeH_4 to SnH_4, the protonic acidity increases and the susceptibility to displacement of hydride ion by amide ion decreases.

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reaction 18, because the germanium would become more positive as the number of amino groups increase (inductive effect) and, consequently, more susceptible to nucleophilic attack by amide.[18] From the data in Table II we calculate $k_{18}/k_8 = 0.18$.

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Part II

PREPARATION AND REACTIONS OF POTASSIUM GERMYLTRIHYDROBORATE, $KGeH_3BH_3$

ABSTRACT

Potassium germyltrihydroborate is prepared from the reaction of potassium germyl (in excess) with diborane in 1,2-dimethyoxyethane. It is catalytically rearranged by diborane to form unstable products which subsequently decompose into a germanium hydride polymer and potassium tetrahydroborate. It is relatively stable in alkaline solutions, hydrolyzes slowly in neutral solutions and hydrolyzes rapidly in acidic solutions to form germane and hydrogen in a 1 to 3 ratio. It is thermally decomposed above its melting point of 98.0-99.0° into a germanium hydride polymer and potassium tetrahydroborate.

The infrared and proton magnetic resonance spectra are given.

A. Introduction

Although there are many organoboranes, there are very few compounds containing a silicon-boron bond, and even fewer containing a germanium-boron bond. Amberger and Römer[1] reported the preparation of a series of compounds containing the silicon-boron bond from the metathetical reactions of potassium silyl with monochloroboranes containing at least one boron-nitrogen bond. Of these compounds, only $H_3SiBH_2N(C_2H_5)_3$ is nearest to a compound in which the silicon and boron are completely hydrogenated. These compounds were colorless liquids which decomposed slowly at room temperature. Nöth and Höllerer[2] also reported the preparation of a similar series of silicon-boron compounds from metatheses using alkali metal organosilyl reactants. These organosilyl compounds were more stable than the silyl compounds. Some borazoles containing organosilyl groups[3] have been reported also. The preparations by novel routes of some halogen compounds have been reported. Trichlorosilyldichloroborane[4] was prepared in an electric discharge from tetrachlorodiboron and glass, and several fluorosilylfluoroboranes[5] were prepared from the reaction of silicon difluoride with boron trifluoride. With respect to hydroborates, lithium trichlorosilyltrihydroborate and lithium pentachlorodisilanyltrihydroborate were reported formed in the reaction of lithium tetrahydroborate with silicon tetrachloride at low temperatures,[6] and lithium triphenylsilyltriphenylborate[7] was reported prepared from the reaction of lithium triphenylsilyl and triphenylborane. An attempt to prepare potassium silyltrihydroborate from the reaction of potassium silyl with diborane was not successful.[8]

Proceeding to the few compounds containing the germanium-boron bond, lithium triphenylgermyltriphenylborate[7] was reported formed in the reaction

of triphenylborane with lithium triphenylgermyl. A substance[9] containing a germanium-to-boron ratio of 3 to 1 formed when sodium triphenylgermyl was allowed to react with boron trichloride. The germyltrihydroborate anion, $GeH_3BH_3^-$, was postulated as a possible product in the complicated reaction of sodium tetrahydroborate with hexachlorodigermane.[10] This latter indication of a germyltrihydroborate anion prompted us to investigate the reaction of potassium germyl with diborane even though the potassium silyl-diborane reaction was not successful. The investigation was fruitful, for we prepared potassium germyltrihydroborate.

B. Experimental

1. General

Standard vacuum line techniques were employed in handling volatile materials. Non-condensible gases were collected and measured using a Toepler pump. Potassium germyltrihydroborate was handled in a polyethylene dry bag filled with dry argon or nitrogen.

The 1,2-dimethoxyethane was dried with sodium-potassium alloy and degassed before using by distilling it into a -78° trap (dry ice slush) while pumping. Diethyl ether (anhydrous, Allied Chemical) was dried with sodium diphenylketyl[11] and subsequently degassed by distilling it into a -196° trap (liquid nitrogen) while pumping. Diethyl ether was used directly from the bottle in the glove bag. Potassium was distilled directly into the reactor *in vacuo*. Germane[12] and diborane[13] were prepared and purified by standard methods.

The identity and purity of the materials were determined by infrared spectrometry with Perkin-Elmer Infracord spectrophotometers (Model 137B and 137), by mass spectrometry with a Consolidated Engineering Corporation Mass Spectrometer Model 21-620, by proton magnetic resonance with a

Varian High Resolution Nuclear Magnetic Resonance Spectrometer Model HA-100, by molecular weight determinations, and by vapor pressure measurements.

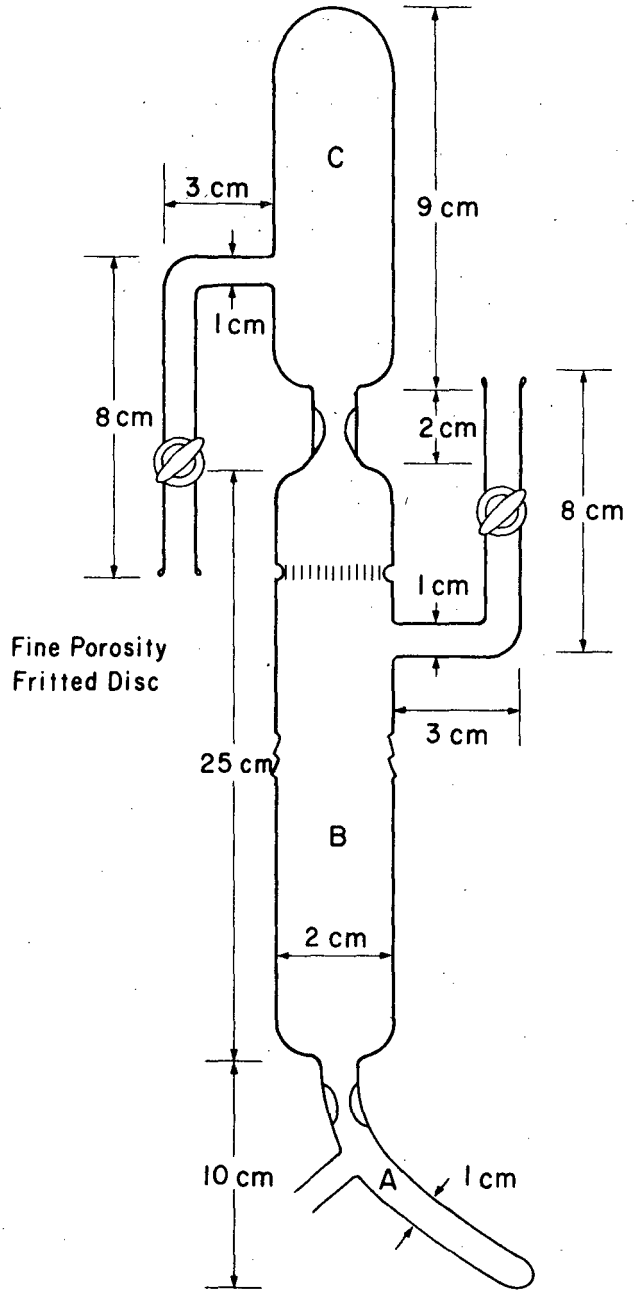
2. Reaction Apparatus

A typical reaction apparatus is illustrated in Fig. 1. The potassium still, A, was constructed from a bent 1 × 11-cm Pyrex tube and connected to B via a thick-walled constriction. The inlet tube was sealed after the introduction of the potassium. Potassium germyl was prepared in B which consisted of a 2 × 25-cm Pyrex tube, a fine porosity fritted glass disc and a stopcock. The reaction mixture was filtered into C which was constructed from a 2 × 9-cm Pyrex tube and stopcock and connected to B via a thick-walled constriction. In the experiment in which the by-products were isolated, two more vessels in series separated with thick-walled constrictions were connected between B and C. These vessels were similar to B except an inlet side-arm was attached to the tube at right-angles to the stopcock side-arm, and they were arranged so that a sequence of reactions and filtrations could be accomplished. The vessel connected to B will be designated as vessel I, and the vessel between vessel I and C will be designated as vessel II.

C. Results and Conclusions

1. Preparation of Potassium Germyl,^{14} an Example

Crude potassium was placed in A and subsequently distilled into B, and then A was removed. In order for the reaction to proceed at a reasonable rate, it was necessary to have as large a surface area of potassium as convenient, covered completely with solvent. Dimethoxyethane (1.8 ml) and 2.203 mmoles of germane were successively condensed into B,



XBL 675-4054

Fig. II-I Typical reaction apparatus

previously cooled to -196°. The reaction mixture was allowed to warm rapidly to about -63° (dimethoxyethane melts at -78°), and then B was kept in a -63.5° bath (chloroform slush) for about 36 hours during which time the reaction was completed. Although a potassium-dimethoxyethane mixture is normally blue at -63.5°, there was no blue coloration during the reaction which visibly occurred on the surface of the metal as evidenced by effervescence on the surface. A very small amount of black precipitate formed during the reaction. B was cooled to -196°, and 0.226 mmole of hydrogen was removed. The reactor was then allowed to warm to -78° while opened to -160° (isopentane slush) and -196° traps in series. The excess germane (1.768 mmoles) was collected in the -196° trap. Potassium germyl was formed according to the following equation, theoretical H_2: 0.218 mmole.

$$e^- + GeH_4 \rightarrow GeH_3^- + 1/2H_2$$

The potassium germyl solution was allowed to warm to room temperature and was subsequently filtered. Any material on the walls was washed down by refluxing the dimethoxyethane. The colorless filtrate was cooled to -196°, and 0.014 mmole of hydrogen evolved while filtering (from the decomposition of potassium germyl) was removed. The constriction was closed, and the two vessels were separated. Only a trace of hydrogen was liberated from the black precipitate when B was heated in a 90° water bath for about an hour. Water (2 ml) was distilled into B, previously cooled to -196°. The precipitate dissolved at room temperature forming a colorless solution and liberating only a trace amount of hydrogen. The filtrate in C was treated with water as above; and after a few minutes at room temperature, C was opened to -160° and -196° traps in series.

Germane (0.444 mmole) was collected in the -196° trap, theoretical: 0.435 mmole.

$$GeH_3^- + H_2O \rightarrow GeH_4 + OH^-$$

While filtering and washing, the small amount of dried potassium germyl splattered on the walls turned yellow rapidly and evolved hydrogen very slowly at room temperature. However, the dried material which was washed down immediately redissolved. But with longer standing, the color darkened, and the material became insoluble. If the black precipitate were a germanium hydride[15,16] and/or potassium hydride[17] (as in the preparation of potassium silyl[8]), the amount was insignificant since only trace amounts of hydrogen were liberated from the solid. On the other hand, it could have been a product from a reaction of hot potassium with glass, and then the hydrogen could have come from trace amounts of potassium germyl unremoved from B.

2. Preparation of Potassium Germyltrihydroborate

Potassium germyl (1.14 mmoles) was prepared, and the solution was filtered. The amount of hydrogen evolved while filtering was 0.018 mmole. The constriction was closed, and B was removed. Diborane (0.550 mmole) was condensed onto the filtrate in vessel I at -196°. Vessel I was allowed to warm until the dimethoxyethane solution melted, and then it was kept in a -78° bath for about 15 minutes with occasional shaking. The cloudy reaction mixture formed was allowed to warm to room temperature and was filtered. The constriction was closed, and vessel I was removed. A 1 M hydrochloric acid solution (3 ml) was distilled onto the white solid in vessel I at -196°, and the mixture was allowed to warm to and was kept at room temperature for a few minutes. The amount of hydrogen evolved

was 0.535 mmole, corresponding to 0.134 mmole of potassium tetrahydroborate.[18] The white solid was found to be potassium tetrahydroborate in a separate experiment, described later. Vessel II was kept at room temperature for about two hours. During this time, there was no visible precipitation, and only trace amounts of germane and hydrogen were evolved. The dimethoxyethane was distilled into a -196° trap, and the vessel at room temperature was kept opened to the -196° trap for 30 minutes. During this time, the white residue turned partially yellow, and 0.103 mmole of germane and a trace of hydrogen were evolved. Diethyl ether (2.1 ml) was distilled into the vessel. The mixture was kept at room temperature for about 30 minutes and then filtered. The yellow and white residue left on the filter did not redissolve in dimethoxyethane. The amount of hydrogen evolved in this step was 0.014 mmole. The constriction was closed, and the two vessels were separated. The ether was removed from C yielding a white solid, potassium germyltrihydroborate. Vessel II, containing the yellow and white residue, was heated with a low flame until gas evolution ceased. In the succeeding experiments, the temperature was noted. A trace amount of condensible gas and 0.128 mmole of hydrogen were evolved, and the white and yellow residue turned black with no melting. The black solid was treated with a ca. 1 M hydrochloric acid solution as above. No condensible gases were liberated, 0.525 mmole of hydrogen was evolved, and the black solid did not dissolve. An ether solution of the final white solid, potassium germyltrihydroborate, was treated with a ca. 1 M hydrochloric acid solution as above. Germane (0.813 mmole) and 2.44 mmoles of hydrogen were collected, corresponding to 0.813 mmole of potassium germyltrihydroborate. When hydrolyzed, potassium germyltrihydroborate was found to

quantitatively evolve germane and hydrogen in a 1 to 3 ratio. The total amount of hydrogen possible from the amounts of potassium germyl and diborane used was 3.360 mmoles, whereas the amount recovered was 3.336 mmoles (in the form of hydrogen and germane).

The main reaction was the formation of potassium germyltrihydroborate.

$$KGeH_3 + 1/2B_2H_6 \rightarrow KGeH_3BH_3 \qquad (1)$$

However, there was a catalyzed secondary reaction involving the formation of potassium tetrahydroborate and presumably the unstable potassium digermanyltrihydroborate. More information on the secondary reaction is given in the following sections.

$$2KGeH_3BH_3 \xrightarrow{B_2H_6} KBH_4 + KGe_2H_5BH_3 \qquad (2)$$

Potassium digermanyltrihydroborate seems to be stable in solution, as evidenced by no more precipitation and trace amounts of gas evolution when the filtrate was kept at room temperature for two hours. But with dimethoxyethane removal, it decomposed with the evolution of volatile hydrides and hydrogen while it turned partially yellow. The solid residue appears to be polymeric since it did not redissolve in dimethoxyethane. This decomposition involved the formation of potassium tetrahydroborate and a germanium hydride polymer.[15]

$$KGe_2H_5BH_3 \longrightarrow 2/x(GeH_2)_x + KBH_4 \qquad (3)$$

The hydrogen and volatile hydrides evolved with dimethoxyethane removal, filtrate of the ether mixture, and subsequent heating came from the decomposition of the polymer[15] and excess potassium germyl[16]

($KGeH_3 \rightarrow KGe + 3/2H_2$). Potassium tetrahydroborate has been reported to decompose at about 500°.[19] The theoretical amount of hydrogen is 0.329 mmole (based on the difference between the amount of potassium germyltrihydroborate and twice the amount of diborane), whereas that found (in the form of H_2 and GeH_4) was 0.348 mmole. From reactions 2 and 3, the amounts of potassium tetrahydroborate formed initially and during the decomposition should be equivalent which they are, 0.134 mmole versus 0.131 mmole (corresponding to 0.525 mmole of hydrogen liberated from the hydrolysis of the heated product). However, these values are slightly below that expected (0.143 mmole).

In a similar experiment except there was no separation of the by-products 2.08 mmoles of diborane was allowed to react with an unfiltered potassium germyl (4.26 mmoles) solution as above. With the removal of the dimethoxyethane and subsequent treatment as before, 0.0447 mmole of hydrogen was evolved as well as volatile hydrides which were fractionally distilled by passing them through -95° (toluene slush), -160° and -196° traps. A trace amount of digermane was collected in the -160° trap and 0.675 mmole of germane in the -196° trap. Diethyl ether (7.5 ml.) was condensed onto the yellow and white solid. The amounts of hydrogen and germane evolved while filtering were 0.017 mmole and 0.041 mmole, respectively. After separating B from C, B was heated at about 200° in an oil bath until the gas evolution ceased. The yellow and white solid turned black, and 0.008 mmole of germane and 0.577 mmole of hydrogen were evolved. Treatment of the black solid with 3 ml of a ca. 1 M hydrochloric acid solution liberated 6.66 mmoles of hydrogen. The diethyl ether was removed from the filtrate in C which was then opened in the dry bag. About 2 mmoles of potassium germyltrihydroborate was recovered. The ratio of

the amount of hydrogen evolved with hydrolysis to the sum of the amounts of hydrogen (corrected for the excess potassium germyl) and the equivalent in the volatile hydrides evolved with dimethoxyethane removal, filtration of the ether mixture and heating was 3.42 compared to 3.47 in the preceding experiment.

3. Identification of Potassium Tetrahydroborate as a By-Product

The same procedure was followed as in the experiment where the by-products were separated except vessel I was opened in a dry bag, and x-ray powder samples were prepared. The x-ray powder pattern was obtained by Mrs. Helena Ruben (Lawrence Radiation Laboratory, Berkeley) and was found to be that of potassium tetrahydroborate, by comparison of the pattern with that of an authentic sample of potassium tetrahydroborate.

4. Reaction of Dilute Hydrochloric Acid with the Reaction Mixture of Potassium Germyl (in Excess) and Diborane

Diborane (0.667 mmole) was allowed to react with an unfiltered potassium germyl (1.348 mmoles) solution as before, except the reaction mixture was kept at room temperature for about five minutes (after being kept at -78° for 15 minutes) and then cooled to -196° instead of filtering. A ca. 1 M hydrochloric acid solution (3 ml) was condensed onto the solid, and the mixture was allowed to warm to room temperature and kept at this temperature until the effervescence ceased (about 30 minutes). The volatile products were fractionated through -78°, -95°, -160° and -196° traps, yielding 4.17 mmoles of hydrogen, 0.991 mmole of germane in the -196° trap, 0.164 mmole of digermane in the -160° trap and a trace amount of trigermane in the -95° trap. The evolution of trigermane suggests the formation of potassium trigermanyltrihydroborate.

$$3KGeH_3BH_3 \xrightarrow{B_2H_6} 2KBH_4 + KGe_3H_7BH_3 \qquad (4)$$

Since trigermane has a low volatility,[12] complete removal from the aqueous-dimethoxyethane solution would not be possible. Assuming that the unrecovered germanium is in the form of trigermane, that reactions 1, 2, and 4 occurred and that the hydrolysis of these trihydroborates gives the hydride to hydrogen ratio of 1 to 3, then the theoretical amount of hydrogen evolved with hydrolysis is 4.19 mmoles (the amount of germane was corrected for the excess potassium germyl).

5. Reaction of Potassium Germyl with Excess Diborane

Diborane (0.905 mmole) was allowed to react with an unfiltered potassium germyl (1.498 mmoles) solution as before. A large amount of precipitate was formed. The volatile hydrides and dimethoxyethane removed from B (0.0676 mmole of hydrogen also was evolved) were condensed into a vessel containing about 5 ml of a ca. 1 M hydrochloric acid solution at -196°. After the mixture was at room temperature for a few minutes, the volatile products were removed and fractionally distilled by passing them through -78°, -95°, -160° and -196° traps. Solvent was collected in the -78° trap, 0.0048 mmole of trigermane in the -95° trap, 0.0605 mmole of digermane in the -160° trap and 0.206 mmole of germane in the -196° trap. The amount of hydrogen evolved was 0.654 mmole which corresponds to the 0.109 mmole of excess diborane.[17] Diethyl ether (2.0 ml) was distilled onto the yellow and white residue, and the mixture was filtered during which only a trace amount of hydrogen was evolved. The constriction was closed, and the two vessels were separated. B was heated at about 200°. The yellow and white solid became orange

and then black while 0.907 mmole of hydrogen, a trace amount of dimethoxyethane, 0.0157 mmole of digermane and 0.0194 mmole of germane were evolved. The black solid was treated with a ca. 1 M hydrochloric acid solution as before. The solid did not dissolve, but 5.741 mmoles of hydrogen was evolved. The ether was removed from the filtrate in C leaving a very small amount of white residue, presumed to be potassium germyltrihydroborate. It was completely decomposed by heating up to about 500°. The amount of hydrogen evolved was 0.0477 mmole, corresponding to a 1% yield of potassium germyltrihydroborate. Subsequent treatment with acid liberated no hydrogen. The total theoretical amount of hydrogen possible from the amounts of potassium germyl and diborane used was 4.635 mmoles, and that found was 4.588 mmoles.

The net reaction with excess diborane appears to be the following:

$$KGeH_3 + 1/2B_2H_6 \rightarrow 1/x(GeH_2)_x + KBH_4 \qquad (5)$$

The theoretical amount of hydrogen possible from the polymer is 1.483 mmoles, whereas that found was 1.666 mmoles (in the form of volatile hydrides and hydrogen evolved with dimethoxyethane removal, filtration of the ether mixture and heating). The theoretical amount of hydrogen from the hydrolysis of the potassium tetrahydroborate is 5.932 mmoles, whereas that found was 5.741 mmoles.

In a similar experiment, 0.820 mmole of diborane was allowed to react with 0.690 mmole of potassium germyl as before. The reaction mixture was kept at room temperature (after being kept at -78° for 15 minutes) for about an hour during which a gray precipitate settled. The dimethoxyethane and volatile products were removed and were subsequently

treated with dilute hydrochloric acid as before. The resulting volatile products were fractionated, yielding 2.68 mmoles of hydrogen (corresponding to 0.447 mmole of diborane), 0.107 mmole of germane, 0.0248 mmole of digermane and a trace amount of trigermane. The gray solid left in B turned partially yellow with diemthoxyethane removal. A ca. 1 M hydrochloric acid solution (3 ml) was condensed onto the yellow and gray solid, previously cooled to -196°. The mixture was warmed to room temperature and kept at this temperature for 30 minutes. Effervescence ceased in a few seconds, and there was a large amount of insoluble yellow solid. Germanium hydrides are not readily hydrolyzed.[15] The amounts of hydrogen and germane evolved were 2.78 mmoles and 0.0166 mmole, respectively. Assuming that the germane came from the hydrolysis of undecomposed potassium germyltrihydroborate, then the hydrogen from the hydrolysis of the potassium tetrahydroborate formed according to reaction 5 would be 2.73 mmoles (the theoretical is 2.69 mmoles). The dilute hydrochloric acid was removed from B by distilling it into a -196° trap overnight. With B in series with a -196° trap and the Toepler pump, B was warmed in a 40° water bath for 10 minutes and then with a low flame until gas evolution ceased. The yellow solid became black. The volatile products were fractionated, yielding 0.193 mmole of hydrogen, 0.0616 mmole of germane, 0.0246 mmole of digermane and a trace amount of trigermane. The sum of the amounts of hydrogen and the equivalent in the volatile hydrides evolved with dimethoxyethane removal and heating was 0.678 mmole, whereas the theoretical from the $(GeH_2)_x$ is 0.673 mmole. The gray precipitate was probably polymeric GeH_2 since there was a sufficient amount of excess diborane present to keep all of the potassium tetrahydroborate in solution as potassium diborhohydride.[20,21]

6. Reaction of Dilute Hydrochloric Acid with the Reaction Mixture of Germyl and Diborane (in Excess)

Diborane (0.621 mmole) was allowed to react with an unfiltered potassium germyl (0.621 mmole) solution as before. The reaction mixture was kept at room temperature (after being kept at -78° for 15 minutes) for only 3 minutes and then cooled to -196°. The solution was cloudy at -78° as well as at room temperature. Hydrogen (0.0314 mmole) was removed, and 3 ml of a ca. 1 M hydrochloric acid solution was subsequently distilled onto the mixture. The acidic mixture was allowed to warm to room temperature, whereupon 3.70 mmoles of hydrogen, 0.480 mmole of germane, 0.0656 mmole of digermane and a trace amount of trigermane were evolved. The hydrides were separated by fractional distillation as described before.

The germane evolution suggests the formation of potassium digermyldihydroborate.

$$2KGeH_3BH_3 \xrightarrow{B_2H_6} K(GeH_3)_2BH_2 + KBH_4$$

Potassium digermanyltrihydroborate and trigermanyltrihydroborate were probably formed according to reactions 2 and 4. Since the amount of hydrogen evolved with hydrolysis corresponded to that expected from the hydrolysis of the diborane, no definite conclusions can be drawn.

7. An Attempted N.M.R. Study of a Reaction Mixture of Potassium Germyl and Diborane (in Excess)

Diborane (1.42 mmoles) was allowed to react with 2.10 mmoles of potassium germyl (unfiltered) as before. At -78°, the reaction mixture was cloudy; and with warming to room temperature, a large amount of gray precipitate was formed. After 10 minutes at room temperature, the

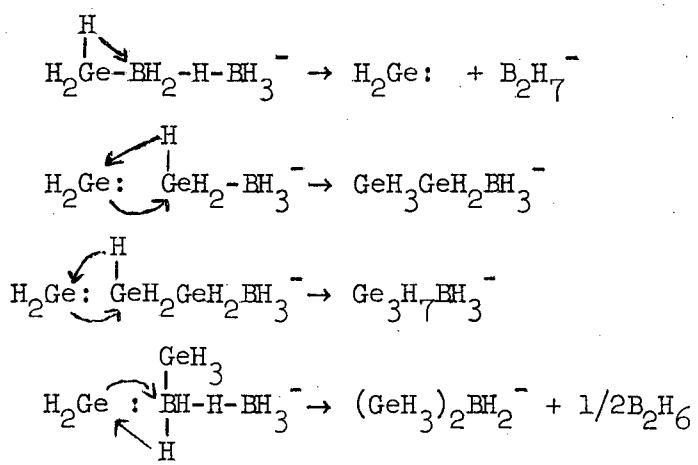
precipitation appeared to have stopped. B was cooled to -196°, and then it was allowed to warm while in series with -78° and -196° traps. About one half of the dimethoxyethane was removed and collected in the -78° trap. It was subsequently recondensed into B. Germane (0.0987 mmole) and 0.286 mmole of diborane (determined from acid hydrolysis as before) were collected in the -196° trap. The reaction mixture was warmed to room temperature and filtered in about 30 minutes. There was very slow precipitation occurring in the filtrate. The solid left on the filter turned a pale yellow. The filtrate was poured into a N.M.R. tube attached to C, and dimethoxyethane was distilled back into C so that the concentration in the tube was adjusted to give about 1.3 M based on the potassium germyl originally used. The N.M.R. tube was sealed and separated from C. The spectrum of the solution showed nothing except the dimethoxyethane peaks, even though there was still some precipitation occurring.

8. Reaction of Potassium Germyltrihydroborate with Diborane

The usual reaction apparatus without A was used, and an inlet tube was attached below the disc for the introduction of 0.137 mmole of potassium germyltrihydroborate. After the potassium germyltrihydroborate was dissolved in 1.3 ml of dimethoxyethane, 0.128 mmole of diborane was condensed into B. The mixture was warmed to room temperature and kept at this temperature for about 10 minutes. A small amount of gray precipitate was formed. The dimethoxyethane and excess diborane were distilled into a -196° trap, and the reactor at room temperature was kept opened to the -196° trap for 15 minutes. The white residue turned partly yellow, while 0.0036 mmole of hydrogen and volatile hydrides were evolved. The dimethoxyethane and volatile hydrides were treated with ca. 1 M

hydrochloric acid solution as before and subsequently fractionated through -78°, -95°, -160° and -196° traps. The amount of hydrogen evolved was 0.738 mmole, corresponding to 0.123 mmole of diborane. Germane (0.0335 mmole) was collected in the -196° trap, 0.0048 mmole of digermane in the -160° trap, and a trace amount of trigermane in the -95° trap. Solvent was trapped at -78°. Diethyl ether (1.5 ml) was added to the yellow and white residue, and the mixture was filtered. The constriction was closed, and the two vessels were separated. B was heated to about 200°, and the solid turned orange, brown and finally black. The amounts of hydrogen and germane evolved were 0.0738 mmole and 0.0036 mmole, respectively. The black solid was treated with a ca. 1 M hydrochloric acid solution as before, and the amount of hydrogen evolved was 0.471 mmole, whereas the theoretical amount is 0.520 mmole (assuming complete transformation to potassium tetrahydroborate). The diethyl ether was removed from C, leaving a white film (presumably potassium germyltrihydroborate). With heating to about 200°, the film turned yellow and then black with the evolution of 0.0072 mmole of hydrogen and a trace amount of germane. With subsequent treatment with a 1 M hydrochloric acid solution, 0.0266 mmole of hydrogen was evolved. The yield of potassium germyltrihydroborate was about 5% (0.007 mmole). The thermal decomposition of potassium germyltrihydroborate will be discussed later. The sum of the amounts of hydrogen and the equivalent in the volatile hydrides evolved with dimethoxyethane removal and heating was 0.166 mmole, whereas the theoretical is 0.130 mmole (assuming complete transformation to $(GeH_2)_x$). The total theoretical amount of hydrogen possible from the amounts of potassium germyltrihydroborate and unrecovered diborane was 0.426 mmole, whereas that found was 0.422 mmole.

According to preceding experiments and this experiment, potassium germyltrihydroborate appears to be catalytically rearranged by diborane into unstable products which subsequently decompose into potassium tetrahydroborate and germanium hydride polymers. In this experiment, quantitative agreement was not as good as in the other experiments where potassium germyltrihydroborate was prepared and rearranged <u>in situ</u>. A possible mechanism for this catalysis involves the diborohydride anion and germanium dihydride monomer.



Potassium diborohydride is soluble in dimethoxyethane and loses diborane to form potassium tetrahydroborate with dimethoxyethane removal.[20,21] The anions would then decompose with solvent removal or standing by transfer of a hydrogen atom from the germanium to the boron. Even with a slight excess of potassium germyl, there was some catalyzed rearrangement since the reaction mixture was not homogeneous and local regions of excess diborane occurred.

9. Melting Point and Thermal Decomposition of Potassium Germyltrihydroborate

In Run 1, potassium germyltrihydroborate (0.220 mole) was placed in a reactor similar to C. The reactor was placed in a heated oil bath containing a magnetic stirring bar and a thermometer. At 97.5-99.0°, the potassium germyltrihydroborate melted, forming a grayish thick oil and evolving no gases. In sealed melting point tubes filled with argon, the melting point was 98.0-99.0° (uncorrected). At about 135°, the liquid turned light yellow with vigorous effervescence; and at about 142 , it became orange. A red solid was formed at 149° and it turned black at about 160°. The reactor was heated at 160° for three 30-minute intervals. After each interval, the reactor was cooled to -196°, and the hydrogen was measured. After the third interval, hydrogen was still being evolved very slowly. The total amount of hydrogen evolved during these intervals was 0.0724 mmole. The temperature of the bath was increased to about 200° and the heating was continued until no more hydrogen was evolved, about 5 minutes. The amount of hydrogen evolved in this step was 0.0108 mmole. The condensible gases evolved with the hydrogen were separated by fractional distillation. Germane (0.0581 mmole) was collected at -196°, 0.0102 mmole of digermane at -160°, and 0.0036 mmole of trigermane at -95°. The black solid was then treated with a ca. 1 M hydrochloric acid solution as before and 0.849 mmole of hydrogen was evolved. The black solid did not dissolve in the acid. The hydrogen material balance was 0.660 mmole calculated and 0.668 mmole found.

In Run 2, the same procedure as above was used except the final black solid was not treated with dilute hydrochloric acid. The reactor was opened in the dry bag, and x-ray powder samples of the black solid were

prepared. The pattern was obtained by Mrs. Helena Ruben and was found to be potassium tetrahydroborate. The total amount of hydrogen evolved while heating was 0.0310 mmole. The condensible gases were fractionated, yielding 0.0242 mmole of germane, 0.0061 mmole of digermane and a trace amount of trigermane. The amount of potassium germyltrihydroborate used was 0.0880 mmole.

It appears that potassium germyltrihydroborate is thermally rearranged into potassium tetrahydroborate and presumably $(GeH_2)_x$ which is subsequently decomposed into hydrogen, germanium and volatile hydrides (characteristic of germanium hydride polymers[15]).

$$KGeH_3BH_3 \xrightarrow{\Delta} 1/x(GeH_2)_x + KBH_4$$

The theoretical amount of hydrogen with hydrolysis is 0.880 mmole, whereas that found was 0.849 mmole. The theoretical amounts of thermal hydrogen in Runs 1 and 2 are 0.220 mmole and 0.0880 mmole, respectively. The amounts of hydrogen and the equivalent in the volatile hydrides found were 0.244 mmole and 0.0977 mmole, respectively. A possible mechanism is just a hydride transfer from the germanium to the boron to form potassium tetrahydroborate and germanium dihydride which polymerizes and/or decomposes.

The low melting point of potassium germyltrihydroborate is unusual for an inorganic potassium salt.[22] The melting without decomposition was totally unexpected since potassium and sodium germyl[16] as well as germanium hydride polymers[15] become yellow and brown and evolve hydrogen near room temperature. Most boron hydride salts decompose before melting, but their melting points are relatively quite high. For example, lithium, sodium and potassium tetrahydroborate start decomposing at about 280°, 400° and 500°, respectively.[19]

10. Reaction of Potassium Germyltrihydroborate with Dilute Hydrochloric Acid

Potassium germyltrihydroborate (0.111 mmole) was transferred to C, and 3 ml of a ca. 1 M hydrochloric acid solution was distilled onto the solid, previously cooled to -196°. The mixture was allowed to warm to room temperature and was mixed well for about 10 minutes. Effervescence ceased after only about a minute. The volatile products were fractionally distilled into -78° and -196° traps. The amounts of hydrogen and germane collected were 0.337 mmole and 0.112 mmole, respectively. The theoretical amounts are 0.333 mmole and 0.111 mmole.

$$KGeH_3BH_3 + H^+ + 3H_2O \longrightarrow K^+ + GeH_4 + B(OH)_3 + 3H_2$$

11. Reaction of Potassium Germyltrihydroborate with Oxygen

A sample of potassium germyltrihydroborate was kept in contact with oxygen (Matheson Co., Inc.) at room temperature for 15 minutes. There was no visible change in the white solid, and all of the oxygen was recovered.

12. Reaction of Potassium Germyltrihydroborate with Water

Water (2 ml) was distilled onto 0.750 mmole of potassium germyltrihydroborate in C, cooled to -196°. C was allowed to warm to room temperature and kept at this temperature for 30 minutes. A very small amount of gray solid did not dissolve. The volatile products were fractionated through -78° and 196° traps. Germane (0.015 mmole) and 0.024 mmole of hydrogen were collected. During two hours more at room temperature, 0.041 mmole of germane and 0.069 mmole of hydrogen were evolved. Only 7.5% of the potassium germyltrihydroborate was hydrolyzed over 2-1/2 hours at

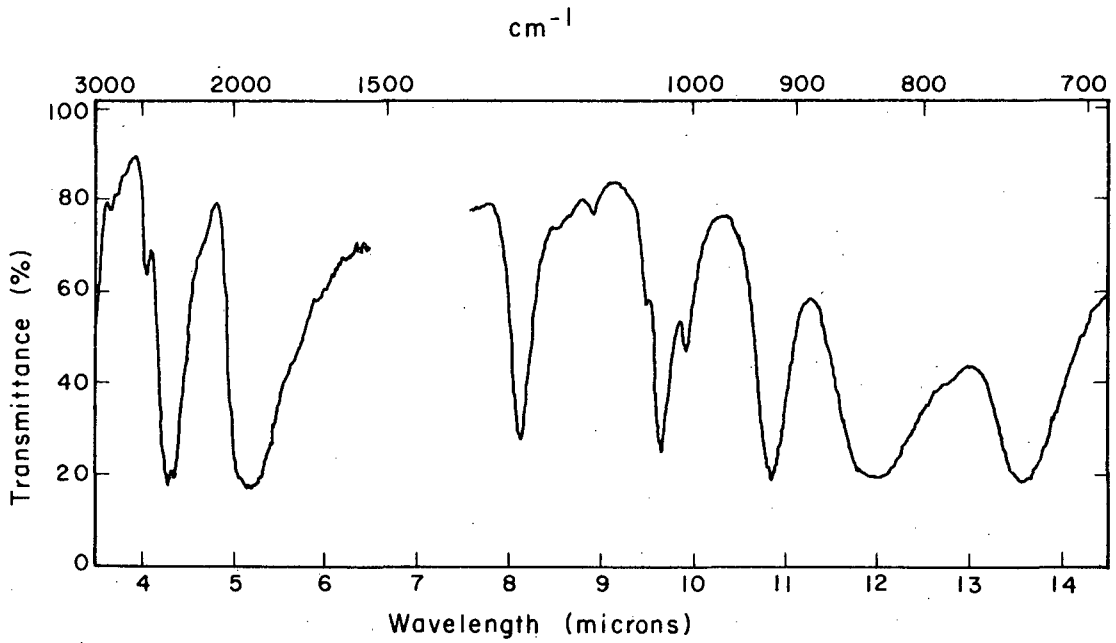
room temperature. Potassium germyltrihydroborate rapidly deliquesces in moist air.

13. Reaction of Potassium Germyltrihydroborate with Aqueous Sodium Hydroxide

Potassium germyltrihydroborate (0.690 mmole) was transferred to C, and 3 ml of a ca. 0.2 M sodium hydroxide solution was added by filling the vacuum line adaptor attached to the stopcock with the solution and by opening the stopcock so the solution would flow into C, previously cooled to -196°. Care was taken to leave some of the solution in the adaptor, so no air would get into C. The mixture was warmed to room temperature and kept at this temperature for 10 minutes. During this time only 0.007 mmole of hydrogen and a trace amount of germane were evolved. The potassium germyltrihydroborate dissolved readily.

14. Infrared Spectra of Potassium Germyltrihydroborate

The spectra are presented in Figures 2 and 3. A nujol mull was used, and the nujol peaks (3000 cm^{-1}, 1470 cm^{-1}, 1380 cm^{-1}) have been left blank. These peaks were identical in shape to those obtained from pure nujol. There is no evidence for potassium tetrahydroborate being present.[23] The absorptions due to the $-BH_3$ group compare very well with the absorptions in the spectra of aminoboranes[24] and BH_3X^- salts (X = SCN, F, CN).[25] On the other hand, the absorptions due to the $-GeH_3$ group have shifted significantly compared to those for compounds containing the $-GeH_3$ group such as the germyl halides,[26,29] methylgermane,[27,29] and silylgermane.[28,29] Therefore, only partial assignments can be made. The three absorptions at 2475 cm^{-1}, 2340 cm^{-1} and 2290 cm^{-1} could be assigned to the B-H stretching modes. It has been reported[23] that a slurry of lithium methyltrihydroborate absorbes at 2190 cm^{-1} and 2130 cm^{-1}. These were the only



XBL 675-4055

Fig. II-2 Infrared spectrum (4.5 mμ - 14.5 mμ) of potassium germyltrihydroborate.

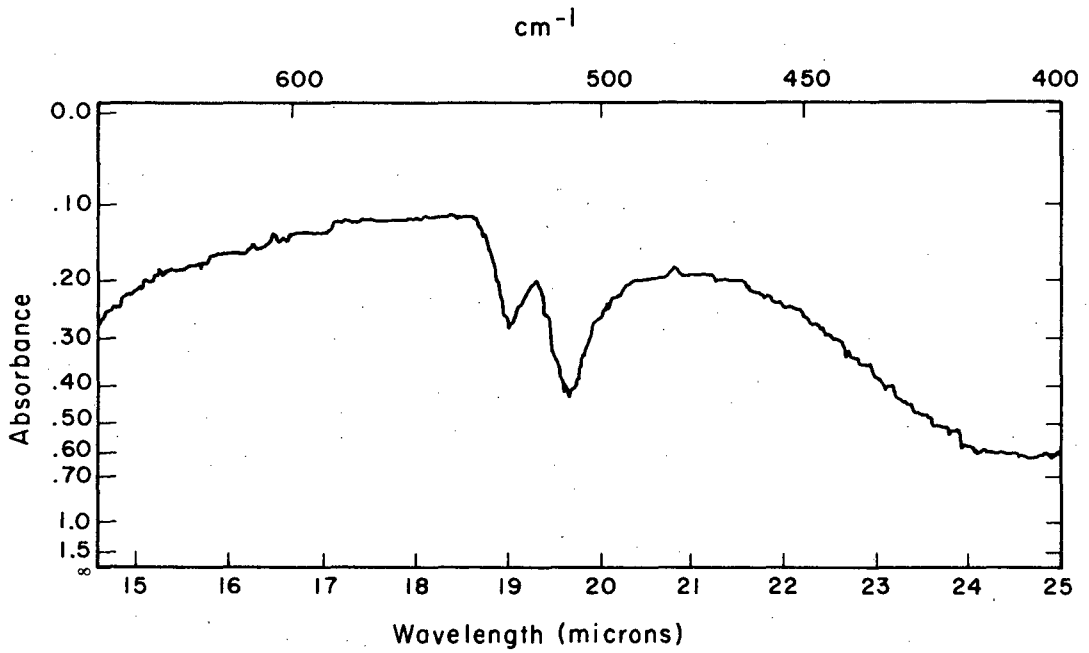


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Fig. II-3 Infrared spectrum (14.5 mμ - 25 mμ) of potassium germyltrihydroborate.

frequencies given. The broad 1930 cm^{-1} absorption is probably due to Ge-H stretching. This has shifted to a lower frequency compared to the usual Ge-H stretching frequency near 2100 cm^{-1} (CH_3GeH_3, 2084 cm^{-1}; GeH_3X, 2112 cm^{-1} to 2132 cm^{-1}; SiH_3GeH_3, 2100 cm^{-1}). The $-BH_3$ deformation absorptions are those in the 1052 cm^{-1} to 1010 cm^{-1} region. The strong absorption at 1230 cm^{-1} might also be a deformation since H_3NBH_3 has a deformation frequency at 1175 cm^{-1}. The $-GeH_3$ deformation frequencies are probably those in the 922 cm^{-1} to 735 cm^{-1} region. However, in trimethylaminoborane the $-BH_3$ rocking frequency is at 915 cm^{-1}, so the absorption at 922 cm^{-1} could be due to $-BH_3$ rocking. The absorptions at 509 cm^{-1} and 526 cm^{-1} could be due to $-GeH_3$ rocking (CH_3GeH_3 has a rocking frequency at 506 cm^{-1}) and Ge-B stretching. On the other hand, there is a broad band near 400 cm^{-1} which also could be the Ge-B stretching absorption. The Si-B stretching frequency in compounds such as trimethylsilylbis(dimethylamino)borane[2] is near 500 cm^{-1}.

15. Proton Magnetic Resonance Spectrum of Potassium Germyltrihydroborate in Aqueous Sodium Hydroxide

The spectrum is presented in Figure 4. The spectrum was obtained by Mr. Frank Papen (Department of Chemistry, University of California, Berkeley). The p.m.r. samples were taken from the aqueous sodium hydroxide solution discussed above. The spectrum of the germyltrihydroborate anion is that expected for an ion with the structure $H_3Ge-BH_3^-$, in which a germyl group has replaced one of the hydrogen atoms in BH_4^-. Boron has two isotopes of nuclear spins 3/2 (^{11}B, 81.17% abundant) and 3 (^{10}B, 18.83% abundant), so the resonance of the three protons of the $-BH_3$ group is split into a 1:1:1:1 quartet ($J_{^{11}BH}$ = 81 cps, centered at 0.16 ppm to low field of T.M.S.) and into a 1:1:1:1:1:1:1 septet ($J_{^{10}BH}$ = 27 cps). Each line

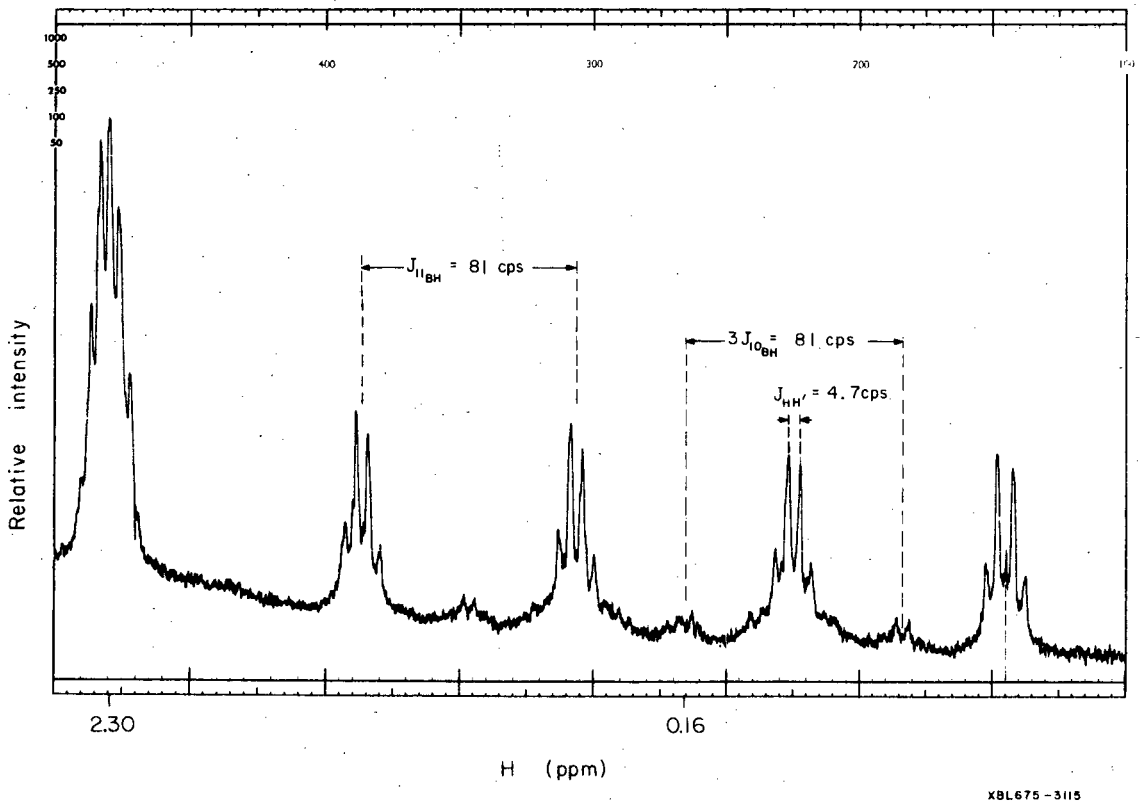

Fig. II-4 Proton magnetic resonance spectrum of potassium germyltrihydroborate at 100 Mc/sec with a sweep width of 500 cps.

of the quartet and septet is split by the three protons of the $-GeH_3'$ group into a 1:3:3:1 quartet ($J_{HH'}$ = 4.7 cps). The $-GeH_3'$ resonance (centered at 2.30 ppm to low field of T.M.S.) is split by the three protons of the $-BH_3$ group as well as by the boron isotopes. From $J_{HH'}$ = 4.7 cps and neglecting $J_{^{10}BH'}$, $J_{^{11}BH'}$ was calculated from the weighted average of the shifts of the components of each peak relative to the center peak and was found to be 2.9 cps. The calculated shifts and weighted averages are presented in Table I.

Table I. Calculated Shifts and Weighted Averages, Relative to Center Peak

Calculated Shift Relative to Center Peak, cps	Weight	Calculated Weighted Average, cps	Observed, cps
2.0	3/7		
3.8	3/7	3.3	3.3
5.6	1/7		
6.7	3/4	7.2	7.5
8.5	1/4		6.8
11.4	1	11.4	10.5

16. Reaction of Potassium Germyl with Dihydrodiammineboron(III) Tetrahydroborate in Liquid Ammonia

This reaction was investigated to see if the ammonia groups could be displaced by germyl groups to form potassium digermyldihydroborate. Diborane (0.698 mmole) was condensed into B at -196° containing a potassium

germyl[30] (1.475 mmoles)-ammonia solid at -196°. B was removed from the -196° bath and immediately placed in a -130° bath (n-pentane slush) which was then allowed to warm to -108° over three hours in order to prepare the "diammoniate".[31] The reaction mixture was then allowed to warm to just above the melting point of ammonia (about -77°) and kept at this temperature for three hours. During this time a trace amount of hydrogen and 0.558 mmole of germane were evolved. The reaction mixture was allowed to warm to -23° and kept at this temperature for an hour during which the germane (0.226 mmole) and hydrogen (0.027 mmole) evolution ceased, and the solution became cloudy. The "diammoniate" is too acidic[32] as evidenced by germane evolution (the theoretical amount of germane is 0.698 mmole).

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